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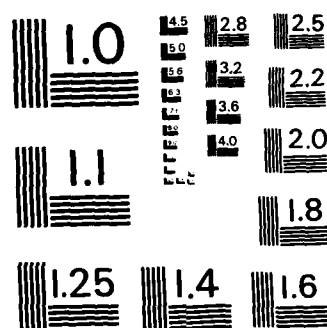
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Complex Molecular Motions in Bulk Hard Segment

Polyurethanes - A Deuterium NMR Study

by

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)  Solid state deuterium NMR spectroscopy is used to characterize molecular motion in two specifically deuterated polyurethane hard segment polymers. The polyurethanes consist of 4,4'-diphenylmethane diisocyanate (MDI) chain extended with [2,2,3,3-d <sub>4</sub> ] butanediol (BDO), and 2,4 toluene diisocyanate (TDI) chain extended with [2,2,3,3-d <sub>4</sub> ] butanediol. Lineshape and relaxation (T <sub>1</sub> ) data were obtained as a function of temperature. The results indicate a broad distribution of motional correlation times, in both materials. In the semicrystalline		

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**Complex Molecular Motions in Bulk Hard Segment  
Polyurethanes - A Deuterium NMR Study**

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111

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# ABSTRACT

Solid state deuterium NMR spectroscopy is used to characterize molecular motion in two specifically deuterated polyurethane hard segment polymers. The polyurethanes consist of 4,4'-diphenylmethane diisocyanate (MDI) chain extended with [2,2,3,3- $d_4$ ] butanediol (BDO), and 2,4 toluene diisocyanate (TDI) chain extended with [2,2,3,3- $d_4$ ] butanediol. Lineshape and relaxation ( $T_1$ ) data were obtained as a function of temperature. The results indicate a broad distribution of motional correlation times, in both materials. In the semicrystalline MDI-BDO polymer, the distribution divides cleanly into two components that are attributable to the crystalline and amorphous regions of the material. In the TDI-BDO polymer, there is only a single broad distribution in keeping with the completely amorphous nature of this material. The results also show that the predominant large-scale motion of the alkyl chain is a gauche-trans conformational hop. The central methylene carbons of the butanediol undergo librations about their equilibrium positions, in addition to the large scale conformational transitions. Above  $\sim 60^\circ\text{C}$ , additional larger-scale diffusion of the entire butanediol moiety occurs within a cone of semiangle  $\sim 15^\circ$ . The results are consistent with the existence of kinked conformations in the alkyl chain of this material.

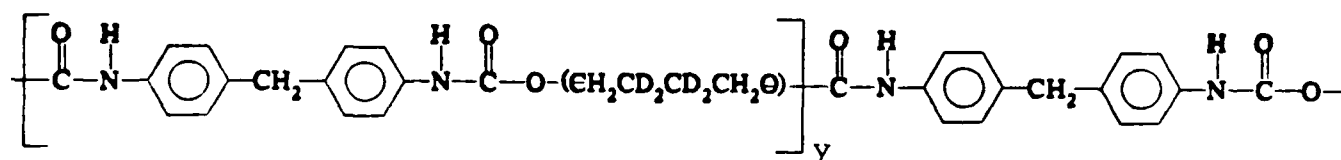
The morphology and physical properties of polyurethane block copolymers have been areas of considerable interest for at least 20 years. Studies of these thermoplastic elastomers have focussed primarily on the microphase separation of the hard and soft segments into domains, to which the unique properties of these materials may be directly ascribed.

We have recently demonstrated the viability of solid state deuterium ( $^2\text{H}$ ) NMR as a technique for evaluating phase separation and phase mixing in polyurethanes,<sup>1</sup> and in another segmented copolymer system, the Hytrel copolyesters.<sup>2,3</sup> The NMR method is based on differential segmental mobilities of  $^2\text{H}$ -labeled moieties in the hard and soft domains and at the domain interfaces.

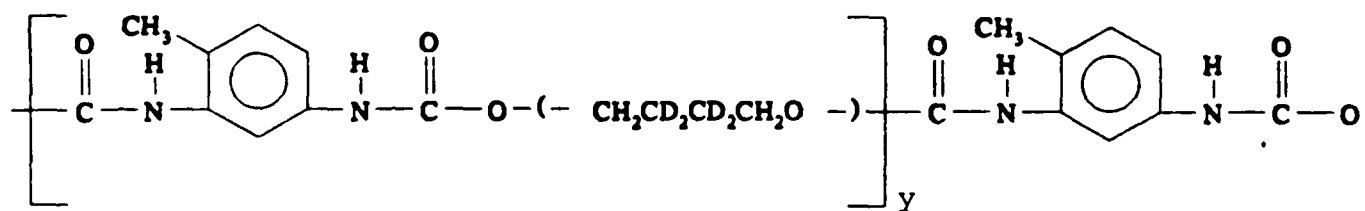
Solid state  $^2\text{H}$  NMR is a powerful tool for characterizing molecular motion in polymers.<sup>4,5</sup> In a rigid lattice powder, where the orientation of a selected C-D bond is random and the motions of this bond are slow on the  $^2\text{H}$  NMR timescale ( $\tau_c \geq 10^{-3}$  sec), the  $^2\text{H}$  NMR spectrum consists of a Pake doublet that has a quadrupole splitting,  $\Delta\nu_Q$ , of  $\sim 128$  kHz. The broad spectrum arises from the interaction of the quadrupole moment of the deuteron and the electric field gradient around the nucleus. The electric field gradient tensor is axially symmetric, and has its maximal component along the C-D bond axis. Because of this, the interpretation of  $^2\text{H}$  NMR lineshapes in the presence of motion is straightforward. The spectra are sensitive to the nature of the motion (e.g. diffusive or discrete hops), the geometry of the motion, and the correlation time of the motion when the correlation time is in the intermediate exchange regime ( $10^{-7}$  s  $< \tau_c < 10^{-4}$  s).<sup>4,5</sup> Therefore, temperature-dependent solid state  $^2\text{H}$  NMR spectra can provide information concerning the rate, angular range, and nature of the motion. It is clear that information of this type is essential to obtaining a precise correlation of polymer molecular structure and observed macroscopic properties.



We report here results of a  $^2\text{H}$  NMR study of molecular motion in two polyurethanes consisting entirely of hard segments. The materials are 4,4'- diphenylmethane diisocyanate (MDI) chain extended with [2,2,3,3- $d_4$ ] butanediol (BDO); and 2,4-toluene diisocyanate (TDI) chain extended with [2,2,3,3- $d_4$ ] butanediol. The structures are shown below.



MDI-BDO



TDI-BDO

The deuterium label is located only on the center methylene carbons of the butanediol residues, and thus our study probes local motions in the vicinity of the label. Earlier studies of poly(butylene terephthalate), which contains the same labeled butanediol moiety, have shown that the predominant motion of the alkyl segment is of a three-bond type resulting in a fast gauche-trans conformational reorientation of the interior methylenes.<sup>2,6,7</sup> These studies further showed that the terephthalate residues are moving slowly on the  $^2\text{H}$

NMR timescale.

In this paper we address the details of molecular motion of the butanediol portion of the polyurethane hard segment. Such experiments are relevant in view of recent SAXS studies on segmented polyurethanes by Koberstein and co-workers.<sup>8,9</sup> Their experiments suggest that the hard segments exist in kinked conformations, and that the hard segment chains are able to fold back on themselves in the solid state, thereby filling space efficiently. The kinks would likely be located at the butanediol moiety which is the most flexible portion of the hard segment chain.

Furthermore, Dumais *et al.*<sup>1</sup> have used deuterium NMR spectra of the MDI-BDO material as a control sample for observing and quantifying the interfacial hard segments in a series of polyurethane copolymers containing 70, 60, and 50 wt% MDI-BDO hard segment. They observed that the all-hard segment material exhibits a motionally averaged deuterium NMR lineshape at room temperature, and it was assumed that the molecular motions of the all-hard segment material are similar to those of the hard segment-rich microdomains in the copolymers. However, the details of the hard segment motion were not investigated.

Here we provide experimental data that bear on the following questions related to molecular motion of the butanediol portion of the polyurethane hard segments: (1) What are the predominant modes of molecular motion of the alkyl residues? (2) Are these motions characterized by a single correlation time, or rather by a distribution of characteristic frequencies? (3) How do the dynamics of the butanediol residues in MDI-BDO and TDI-BDO compare? and (4) Are these results consistent with the proposed model of a kinked conformation for the butanediol group?

## EXPERIMENTAL SECTION

*Sample:* The selectively labeled hard segment polyurethane samples were prepared in THF solution according to literature methods,<sup>10</sup> using [2,2,3,3-d<sub>4</sub>] butanediol (Merck) as the starting diol and the appropriate diisocyanate (MDI or TDI). The polymer was characterized by DSC measurements, and by solution state <sup>2</sup>H NMR spectroscopy.

The DSC measurements of the MDI-BDO sample (heating rate 20°C/min) reveal a small high temperature endotherm at ~213°C which is due to melting of the crystalline component.<sup>11</sup> We did not observe a clear glass transition temperature, although this has been reported to be 109°C.<sup>12</sup> The TDI-BDO polymer is known to have a  $T_g$  of 101°C.<sup>12</sup>

*NMR Measurements:* Solution state <sup>2</sup>H NMR analyses were performed on both Varian XL-200 and JEOL GX-500 spectrometers. The samples were dissolved in DMSO and spectra were obtained both at room temperature and at 90°C. The results attest to the integrity of the labeling pattern and indicate a number average degree of polymerization of ~20 for MDI-BDO and ~22 for TDI-BDO.

Solid state <sup>2</sup>H NMR spectra were obtained on a home-built spectrometer operating at 8.5 Tesla, corresponding to a <sup>2</sup>H resonance frequency of 55.26 MHz. The spectrometer has been described previously.<sup>2</sup> The sample temperature was regulated by using either a heated air flow or a liquid nitrogen boil-off system. The temperature was measured next to the sample by means of a digital thermometer (Omega 2176A) equipped with a copper-constantan thermocouple. Temperatures are considered accurate and stable to ±1°C.

Spectra were obtained in quadrature using the quadrupolar echo pulse sequence  $(90_x - \tau_1 - 90_y - \tau_2)$ ,<sup>13</sup> or some variation thereof.<sup>14</sup> The 90° pulse width was typically 3.3 μsec. 4K data points were collected with a digitization rate of 100 nsec/point. Unless specified otherwise, the delay between the quadrupole pulse pair was set at 30 μsec, which

was ample time for the probe and receiver to recover after the pulses.

Variations of the quadrupole echo pulse sequence were used for spin-lattice relaxation time determinations and for selective observation of a fast (short  $T_1$ ) component. The amorphous quadrupole echo pulse sequence<sup>14</sup> was used for progressive saturation  $T_1$  measurements and for selectively observing the fast component. This sequence consists of a train of  $90^\circ$  pulses to saturate the entire spin system, followed by a delay ( $t_d$ ), followed by the quadrupole echo pulse pair. The delay ( $t_d$ ) was varied over several orders of magnitude for the progressive saturation  $T_1$  experiments; and was set at 100 msec ( $\sim 5 \times T_1$  of the fast component), otherwise. The amorphous inversion-recovery quadrupole echo pulse sequence<sup>14</sup> was used to measure the spin-lattice relaxation time of the short  $T_1$  component. The pulse sequence consists of a saturating train of  $90^\circ$  pulses, followed by a delay to allow the magnetization of the rapidly relaxing amorphous component to recover, followed by a  $180^\circ$  pulse to invert the fast component magnetization, followed by a variable delay, followed by the quadrupole echo pulse pair.

*Data Analysis:* Typically 12-20 points were obtained for either progressive saturation or inversion recovery relaxation experiments. Data out to 100 msec ( $5 \times T_1$  of fast component) were reasonably linear and were analyzed with a non-linear three-parameter fit routine on a Nicolet 1180E computer system, using the NMC program. In some cases linearity was checked by casting the inversion-recovery data in semi-log form. The intensity at each delay time was obtained from the height of the echo, or from integration of the entire lineshape. The results obtained by either method were the same, within experimental error.

The total equilibrium  $^2\text{H}$  NMR spectral intensity data were corrected for the variation of the probe signal intensity response with temperature. The probe response was calibrated

by obtaining a fixed number of scans on a sample of L-d3 Alamine under equilibrium conditions at a variety of temperatures.

Calculated solid state  $^2\text{H}$  NMR spectra were obtained according to the methods described by Mehring.<sup>15</sup> The calculated spectra have been corrected for the effects of pulse power fall-off,<sup>16</sup> and for the effects of motions that occur during the quadrupole echo delay time.<sup>17</sup>

## RESULTS

*$^2\text{H}$  NMR Spectra of MDI-BDO* The  $^2\text{H}$  NMR spectra of the bulk MDI-BDO polymer reflect a very broad distribution of motional correlation times at all temperatures observed ( $-59^\circ\text{C}$  to  $+95^\circ\text{C}$ ). This is clearly demonstrated in Figure 1, where we show spectra obtained using the amorphous quadrupole echo pulse sequence at several representative temperatures. The top row of lineshapes was obtained with an equilibrium delay time of 2-4 s between the saturating pulse train and the quadrupole echo pulse pair. From separate progressive saturation spin-lattice relaxation time ( $T_1$ ) experiments (see below), we estimate that we are observing approximately 90% of the deuterons in the MDI-BDO sample at an equilibrium delay time of 2 s at room temperature.

In the second row, we show spectra that were obtained also using the amorphous quadrupole echo pulse sequence, except that the delay between the saturating pulses and the observe pulses is shortened to 100 ms (160 ms for the  $-45^\circ\text{C}$  spectrum). These lineshapes are plotted on the same vertical scale as the corresponding top row spectra, and it is apparent that there is a considerable loss of intensity due to the saturation of deuterons with relatively long  $T_1$  values. Integration of these spectra shows that at room temperature and above (data up to  $123^\circ\text{C}$ , spectrum not shown), approximately 70% of the deuterons contribute to the short  $T_1$  component. At  $-2^\circ\text{C}$ , the short  $T_1$  component has only  $\sim 64\%$

of the intensity of the equilibrium recycle spectrum; and at  $-45^{\circ}\text{C}$ , this value has decreased to  $\sim 48\%$ . The relative intensity data are listed in Table 1. We note that the total intensity (obtained by integration of the spectra, top row, Figure 1) remains approximately constant from  $-2^{\circ}$  to  $73^{\circ}$ . We observe only a slight decrease in total intensity at  $123^{\circ}$ .

Subtraction of the middle row spectra from the corresponding top row spectra affords the lineshapes of the long  $T_1$  component. These difference spectra are shown in the bottom row. The lineshape at  $-45^{\circ}\text{C}$  can be fit to a calculated rigid-lattice Pake doublet with a quadrupole splitting,  $\Delta\nu_Q$ , of 125 kHz. The difference spectra at  $-2^{\circ}\text{C}$ , and  $22^{\circ}\text{C}$  fit somewhat less well to a rigid-lattice pattern, as there is too much intensity at the center of the experimental lineshape, especially at the higher temperature. As the temperature is increased further, to  $55^{\circ}$  and  $73^{\circ}\text{C}$ , the center of the static-like powder patterns (Figure 1, bottom row) continue to fill in (giving rise to a flat-topped spectrum at  $73^{\circ}\text{C}$ ) while the overall breadth at half-height remains the same. This kind of behavior is observed when the methylene groups undergo gauche-trans conformational transitions (such that the C-D bonds hop between two sites separated by a projected (Newman) angle of  $\sim 120^{\circ}$ ) at a rate that is intermediate on the NMR timescale ( $10^{-4} \text{ s} > \tau_c > 10^{-7} \text{ s}$ ).<sup>2,15</sup> A projected Newman angle of  $120^{\circ}$  corresponds to a dihedral (jump) angle between sites of  $\sim 109^{\circ}$ .

*Motion of the Fast Component of MDI-BDO:* In Figure 2 we show  $^2\text{H}$  NMR spectra of the fast component only, obtained using the amorphous quadrupole echo pulse sequence with a delay of 100 milliseconds, at various temperatures. The lineshapes indicate that the motionally averaged electric field gradient tensor is axially asymmetric, suggesting that the motional process leading to collapse of the static powder pattern has two-fold symmetry.<sup>2,15,18</sup> Furthermore, the overall breadth of the room temperature spectrum is  $\sim 120 \text{ kHz}$ ; which implies that the proposed two-fold hopping motion involves a C-D bond

**Figure 4.** Solid state  $^2\text{H}$  NMR spectra (55.26 MHz) of the hard segment TDI-BDO polymer obtained using the amorphous quadrupole echo pulse sequence. Top row. Spectra obtained with an equilibrium delay time of 2-4 sec after the saturating pulse train. Middle row: Spectra obtained with a delay time of 100-160 msec. Bottom row: Difference spectra of the equilibrium and fast recycle lineshapes. Spectra within a column (a-e) were obtained at the same temperature. The experimental temperatures are (a)  $-53$ , (b)  $-6$ , (c)  $22$ , (d)  $40$ , and (e)  $77^\circ\text{C}$ .

**Figure 5.** Plot of the total equilibrium  $^2\text{H}$  NMR spectral intensity (obtained by integration of the lineshapes) versus the temperature. (a) MDI-BDO, (b) TDI-BDO. The intensity data were corrected for the signal intensity response of the probe as described in the text.

**Figure 6.** Representative  $^2\text{H}$  NMR spin-lattice relaxation data of TDI-BDO. (a) Semilogarithmic plot of the magnetization recovery versus the delay time showing the nonexponential nature of the data. The progressive saturation data were obtained using the amorphous quadrupole echo pulse sequence at  $22^\circ\text{C}$ . The amorphous delay time was varied from 1 msec to 2 sec, by which time magnetization recovery was complete. (b) Arrhenius plot of the natural logarithm of the spin-lattice relaxation time (of the short  $T_1$  component) versus the reciprocal of the absolute temperature. The data were obtained using the amorphous inversion-recovery quadrupole echo pulse sequence with a 100-160 msec delay after the saturating pulse train.

## FIGURE CAPTIONS

*Figure 1.* Solid state  $^2\text{H}$  NMR spectra (55.26 MHz) of the hard segment MDI-BDO polymer obtained using the amorphous quadrupole echo pulse sequence. Top row: Spectra obtained with an equilibrium delay time of 2-4 sec after the saturating "comb" of pulses. Middle row: Spectra obtained with a delay time of 100-160 msec. Bottom row: Difference spectra of the equilibrium and fast recycle spectra. Spectra within a column (a-e) were obtained at the same temperature. The experimental temperatures are (a)  $-45^\circ\text{C}$ , (b)  $-2^\circ\text{C}$ , (c)  $22^\circ\text{C}$ , (d)  $55^\circ\text{C}$ , and (e)  $73^\circ\text{C}$ .

*Figure 2.* Experimental (a-d) and calculated (e-h) solid state  $^2\text{H}$  NMR spectra of the short  $T_1$  component of the MDI-BDO polymer. Spectra (a-d) were obtained with the amorphous quadrupole echo pulse sequence with an amorphous delay time,  $t_a$  of 100 msec at  $22^\circ\text{C}$ ,  $42^\circ\text{C}$ ,  $62^\circ\text{C}$ , and  $83^\circ\text{C}$ , respectively. Spectra (e-h) were calculated as described in the text using quadrupole splittings 120, 118, 107, and 105 kHz respectively.

*Figure 3.* Representative  $^2\text{H}$  NMR spin-lattice relaxation data of MDI-BDO. (a) Semilogarithmic plot of the magnetization recovery versus the delay time showing the non-exponential and biphasic nature of the data. The progressive saturation data were obtained using the amorphous quadrupole echo pulse sequence at  $22^\circ\text{C}$ . The amorphous delay time was varied from 1 msec to 8 sec, by which time magnetization recovery was complete. (b) Arrhenius plot of the natural logarithm of the spin-lattice relaxation time (of the short  $T_1$  component) versus the reciprocal of the absolute temperature. The data were obtained using the amorphous inversion-recovery quadrupole echo pulse sequence with a 100-160 msec delay after the saturation pulses.



at rates very much faster than in the crystalline domain and in the fast limit of the  $^2\text{H}$  NMR timescale ( $\tau_c < 10^{-7} \text{ sec}$ ).

The  $^2\text{H}$  NMR spectra of the amorphous component (obtained with a short delay time) are consistent with the occurrence of *gauche-trans* conformational transitions as the major motional mode. The motion consists of hops of the C-D bonds between two equally populated sites separated by a dihedral angle of  $\sim 114^\circ$ . Observation of this motional mode is consistent with the existence of kinked conformations of the alkyl segment in MDI-BDO and TDI-BDO. Low-amplitude high frequency librations of the methylene groups about their equilibrium position may also occur to account for the small observed narrowing of the quadrupole splitting from the rigid lattice value. This motional model is consistent with the observed magnitude of the  $T_1$  minimum in the amorphous component of MDI-BDO, which indicates that more than one motional mode is contributing to relaxation.

Above  $\sim 60^\circ\text{C}$ , we observe further significant narrowing of the  $^2\text{H}$  NMR lineshapes which indicates the onset of an additional mode of motion. This motion is modeled by diffusion of the butanediol chain within a cone of small semiangle ( $10\text{-}20^\circ$ ). The amplitude of the diffusion and thus the semiangle of the cone is assumed to increase with increasing temperature.

Finally, in the amorphous TDI-BDO polymer we observe the onset of large scale translational motion at rates greater than  $10^5 \text{ sec}^{-1}$  at  $\sim 20^\circ\text{C}$  above the glass transition temperature ( $T_g \sim 41^\circ\text{C}$ ), which results in a decrease in intensity of the quadrupole echo.

refocussing results in a scrambling of the quadropole interaction that each spin "sees". Therefore, refocussing is incomplete and we see echoes with reduced intensity. The spectral intensity decreases with increasing temperature because as the motion speeds up, there is an increased probability that more portions of the polymer chain move and therefore more spins are "scrambled".

## SUMMARY

These  $^2\text{H}$  NMR results show the existence of a broad distribution of motional correlation times in the hard segment (butanediol-labeled) polyurethane polymers. In semicrystalline MDI-BDO, the distribution is divided into two major components corresponding to crystalline and amorphous regions of the polymer. In the crystalline region, the C-D bonds may be considered static on the  $^2\text{H}$  NMR timescale at room temperature. However, relaxation data indicate that there are high frequency librational motions of the labeled methylene groups in these relatively rigid domains. The motional constraints in the crystalline region are not easily relaxed at higher temperatures and the distribution shifts only slowly to higher frequencies with increasing temperature.

In the amorphous regions of MDI-BDO and in the amorphous polymer TDI-BDO, there is a broad range of motional correlation times extending over 5 orders of magnitude. Motion in these domains is considerably faster than in the crystalline domains at room temperature. The correlation times range from  $\sim 10^{-5}\text{sec}$  to  $10^{-9}\text{sec}$ . The constraints responsible for the distribution of motion in the amorphous domains is likely differences in local packing density. These constraints vary readily with temperature so that the distribution moves easily to lower or higher frequencies of motion. Thus at  $-50^\circ\text{C}$ , some of the deuterons in the amorphous region are moving as slowly as those in the crystalline regions; while at about  $70^\circ\text{C}$ , most of the deuterons in the amorphous domain are moving

There is indirect IR spectroscopy evidence that the butanediol chain diffusion occurs at elevated temperatures in MDI-BDO polyurethane.<sup>23,24</sup> The evidence consists of quantification of the free and hydrogen-bonded NH groups and is based on their different vibrational frequencies and extinction coefficients. The results reveal an increase in the amount of free NH groups starting at about 75°C. Large-amplitude diffusion of the butanediol moiety would require disruption of the hydrogen bonds of the NH groups on one chain with the oxygen atoms on the ester groups of adjacent chains. A recent communication has questioned the validity of these IR experiments, however, noting that the IR lineshape changes may be accounted for by frequency shifts and reduction of the extinction coefficients of the hydrogen bonded NH group IR band.<sup>26</sup> These workers attribute the changes in extinction coefficient to a change in the "strength" of the hydrogen bond. It is clear, however, that the stretching of hydrogen bonds due to the proposed diffusion of the butanediol chain in a cone would be expected to modulate the IR properties of the NH region.

*Translational Motion in TDI-BDO Above  $T_g$*  We now address the large decrease in absolute  $^2\text{H}$  NMR spectral intensity that we observe in the TDI-BDO material above its glass transition temperature. This intensity decrease is likely due to the onset of translational motions of the polymer chain.

An understanding of this effect requires a more thorough understanding of the quadrupole echo sequence. During the first RF pulse, the spin magnetization is tilted away from alignment with the static field ( $B_0$ ) until it is in a plane perpendicular to  $B_0$ . After the pulse, the magnetization precesses in the plane under the influence of the quadrupolar interaction. Since every spin "sees" interactions with different magnitudes, the spins dephase. The second RF pulse causes the dephasing to change direction and the spins refocus to form an echo. Translational motion that occurs while the spins are dephasing or

transition of the labeled methylene group. In Fig. 7a, we show in a Newman projection (down the center bond of the butanediol moiety) how this motion occurs. As diagrammed, this motion requires a large-scale reorientation of the ends of the polymer chain which would be energetically unfavorable. Several motional models involving cooperative motion about several bonds have been proposed that avoid this situation. Two of the models, involving motion about three bonds are shown schematically in Fig. 7b. These motions have been shown to occur in poly(butylene terephthalate).<sup>2,6</sup> Similar motions probably occur in these polyurethane systems as well.

The observed gauche-trans conformational transitions in these polyurethanes are quite similar to those observed in poly(butylene terephthalate). There are, however, some important differences. The spectra we observe here are best fit to a calculated lineshape obtained with a dihedral angle of  $\sim 114^\circ$ ; as opposed to the  $102^\circ$  angle that was reported for poly(butylene terephthalate).<sup>2</sup> We note that there is some uncertainty in the determination of this angle in the present study because of the broad distribution of motional correlation times (vide supra). Moreover, the conformational hops occur at a much faster rate in the polyurethane system than in poly(butylene terephthalate). The present results indicate that the average correlation time for this motional process is in the fast exchange limit above  $-2^\circ\text{C}$ . In poly(butylene terephthalate) the fast exchange limit for this motional process occurs at  $\sim 85^\circ\text{C}$ . Furthermore, the results for poly(butylene terephthalate) indicate a much narrower distribution of correlation times than what we observe here for MDI-BDO and TDI-BDO.

The most obvious difference between the two systems is the presence of fast butanediol chain diffusion which occurs in the polyurethane hard segment polymers, and results in significantly narrowed spectra at high temperature. The  $^2\text{H}$  NMR spectra of poly(butylene terephthalate) up to  $85^\circ\text{C}$  suggest that little such motion is occurring in this polymer.<sup>2</sup>

have different lineshapes; again indicating that even in the fast recycle spectra, not all the deuterons are moving at rates in the fast limit of the  $^2\text{H}$  NMR timescale.<sup>17</sup>

The distribution in the characteristic frequencies of motion of the labeled methylene groups in the amorphous regime of the polymer are likely due to variation in the local packing density due to the irregular packing of the polymer in these domains. Alternatively, or in addition to the above reasons, the slower components in the distribution may be attributed to butanediol residues that are in constrained conformations because they are the sites of twists and turns of the polymer chain. We note, however, that the observed broad range of motional correlation times probably represents distributions in the characteristic frequencies of several motional modes (e.g. a large-amplitude two-fold hop and a small-angle vibration). Finally, we note that the constraints resulting in the broad range of correlation times in the amorphous region relax readily with temperature, permitting a facile shift of the entire distribution of motion to higher frequencies.

*Details of Molecular Motion in the Fast Component:* The  $^2\text{H}$  NMR spectra of the fast (amorphous) component of the MDI-BDO and TDI-BDO polymer are consistent with the occurrence of gauche-trans isomerization in the butanediol moiety. Librations of the methylene groups are superimposed on this motion, and at high temperatures, diffusion of the entire butanediol chain may also occur.

This motional model is supported by the  $T_1$  data. The magnitude of the  $T_1$  minimum ( $\sim 20$  msec) of the amorphous component in MDI-BDO suggest that more than one motion contributes to relaxation, since we would expect a much higher or lower  $T_1$  value at the minimum if one process were dominant.<sup>22</sup>

The predominant motion affecting lineshapes is the large-amplitude two-fold hop of the labeled methylene groups. The motion results from a gauche-trans conformational

explained by the fact that MDI-BDO is semicrystalline while TDI-BDO is completely amorphous. The slower moving deuterons with long  $T_1$  values observed in the MDI-BDO material are likely located in the crystalline domains. In these domains, the packing is ordered and consequently denser, making the large amplitude (two-fold hop) motion less likely to occur. The existence of crystalline regions in MDI-BDO also explains the constant long  $T_1$  component (30%) that is observed over a wide range of temperatures. At low temperatures ( $\sim -40^\circ\text{C}$ ) deuterons in both the crystalline and amorphous domain MDI-BDO contribute to the long  $T_1$  component as the motions are slow in both regions. At higher temperatures ( $\sim 20^\circ\text{C}$ ), the motional constraints in the amorphous regions are readily relaxed so that essentially all the deuteron in this domain contribute to the fast recycle spectrum. However, deuterons in the crystalline domains are still packed tightly and therefore move slowly and contribute to the long  $T_1$  component. Our relative intensity results indicate that our MDI-BDO sample is  $\sim 30\%$  crystalline. Although it is difficult to obtain reliable quantitative results from our DSC measurements, 30% crystallinity is not inconsistent with these results. Moreover, it is well known that crystallinity of 30% can be routinely obtained in MDI-BDO.<sup>11</sup>

It is clear that even in amorphous domains of these polymers, there is a very broad distribution of motional correlation times. This is demonstrated most clearly by the  $^2\text{H}$  NMR lineshapes of TDI-BDO (Fig. 4). From the lineshapes and the  $T_1$  data, we estimate that the distribution of motional correlation times in the amorphous regions of MDI-BDO and TDI-BDO spans some five orders of magnitude. Even at high temperatures, when the deuterons in the amorphous regions contribute only to the fast recycle (short  $T_1$ ) spectra, there is still a distribution of motions. This is evident in the imperfections of the fit of the calculated spectra to a single correlation time model. Moreover,  $^2\text{H}$  NMR spectra obtained with different delays between pulses (not shown)

temperatures at which intensity losses are not a problem.) In these experiments, the magnetization recovery was reasonably linear up to the longest delay time used (100-160 msec,  $\sim 4 \times T_1$ ). The results are shown in an Arrhenius plot in Fig. 6b. The  $T_1$  data are summarized in Table 2. Note that the  $T_1$  values of the fast component in TDI-BDO and MDI-BDO are quite similar. Thus, in addition to the similarity in the types of motion of the fast component in both polymers, the rates of motion are quite similar as well.

## DISCUSSION

### *Nature of the Distribution of Motional Correlations Times in MDI-BDO and TDI-BDO:*

The evidence presented in the previous section clearly indicates that there is a broad distribution of motional correlation times in both MDI-BDO and TDI-BDO. The nature of the distribution in the two polymers is quite different, however. First, there are slower motions occurring in MDI-BDO than in TDI-BDO. The spin-lattice relaxation indicate that there are deuterons with much longer  $T_1$  values in MDI-BDO than in TDI-BDO. Second, the distribution of motion in MDI-BDO divides clearly into two major components, while that of TDI-BDO does not. This is indicated by the relative intensities of the equilibrium and fast recycle spectra (Fig. 1, Fig. 4, and Table 1). At low temperatures, both polymer systems have  $\sim 50\%$  of the deuterons contributing to the short  $T_1$  component. As the temperature is increased, the percentage of deuterons contributing to the fast component increases on both systems. At room temperature the relative intensity in the short  $T_1$  component starts to plateau at 70% in the MDI-BDO system, and remains at this value even above the glass transition. In the TDI-BDO system, however, the relative intensity of the fast recycle spectra increases monotonically to a value of 100% at about 60°C.

The differences in the distribution of motion in the two polymers can readily be

distribution, the butanediol residues undergo the same type of motion in TDI-BDO and MDI-BDO. That is, the predominant motion is a two-fold hop between sites of equal probability separated by a dihedral angle of  $\sim 114^\circ$ . The average correlation time of this motion is in the fast limit of the  $^2\text{H}$  NMR timescale ( $\tau_c \leq 10^{-7} \text{ sec}$ ) above  $20^\circ\text{C}$ . Superimposed on the large amplitude motion is a small-amplitude libration of the methylene groups which accounts for the observed motionally narrowed breadth of these spectra ( $\sim 120 \text{ kHz}$ ) from the rigid-lattice value. The additional narrowing of the spectrum at  $77^\circ\text{C}$  is attributed both to larger amplitude librations of the methylene groups about their equilibrium positions and to diffusion of the entire butanediol chain within a narrow cone of semiangle  $\sim 10^\circ$ .<sup>20</sup>

We also note that the variation of the total spectral intensity with temperature (obtained by integration of the equilibrium delay spectra) appears markedly different in the TDI-BDO polymer than in the MDI-BDO material. This is shown graphically in Fig. 5. It appears that the large scale motions that occur above  $T_g$  prevent proper refocussing of the quadrupole echo signal, leading to marked reductions in echo amplitude.

*Spin-Lattice Relaxation Times of TDI-BDO:* Further evidence that there is a broad distribution of correlation times is provided by progressive saturation  $T_1$  results obtained at room temperature, using a variable delay that spanned some four decades (2 sec to 1 msec). The data, shown in Fig. 6a, clearly describes a nonexponential recovery. There are deuterons in some environments that take up to 1 sec to relax, whereas a good proportion of deuterons are fully relaxed by 100 msec. In contrast, progressive saturation data obtained at  $60^\circ\text{C}$  (not shown) indicate that all deuterons obtain equilibrium in 200 msec and the nonexponential nature of the magnetization recovery is not as evident.

We have also obtained  $T_1$  results of the fast component only using the amorphous inversion-recovery quadrupole echo pulse sequence at  $-55$ ,  $-17$ , and  $23^\circ\text{C}$ . (These are



short  $T_1$  component increases monotonically until  $\sim 20^\circ\text{C}$  above the glass transition when essentially 100% of the deuterons are observed with a delay time of 100 msec. This is in sharp contrast to the behavior of the MDI-BDO material where the fraction of deuterons contributing to the short  $T_1$  component was constant at  $\sim 70\%$  from  $20^\circ$  to  $73^\circ\text{C}$ .

In the bottom row, we show difference spectra of the corresponding top and middle row lineshapes. These difference spectra represent the lineshapes of the long  $T_1$  component of the distribution. At  $-53^\circ\text{C}$ , the spectrum fits reasonably well to a rigid lattice Pake doublet with a quadrupole splitting  $\Delta\nu_Q \sim 125\text{ kHz}$ . As the temperature is increased, the center of the pattern fills in to give a nearly flat-topped spectrum at  $22^\circ\text{C}$ . At  $77^\circ\text{C}$ , there is essentially no intensity in the difference spectrum as nearly all the deuterons have very short  $T_1$  values and relax within 100 msec. The overall pattern of change in the difference lineshapes is similar to that of the MDI-BDO polymer, although the changes occur at lower temperatures for the TDI-BDO material. This suggests that as in the MDI-BDO material, the predominant motion of the butanediol residues in TDI-BDO is a two-fold hop between sites separated by a dihedral angle of  $\sim 114^\circ$ , consistent with a gauche-trans conformational transition of the interior methylenes.

This interpretation is supported by the lineshapes of the short  $T_1$  component (Fig. 4, middle row), obtained with a delay time of 100 msec (160 msec for the  $-53^\circ\text{C}$  spectrum). At  $-53^\circ\text{C}$ , the spectrum is nearly flat-topped but retains nearly the same spectral breadth ( $\sim 120\text{ kHz}$ ). As the temperature is increased, the center of the pattern becomes dome-like, indicating that the average rate of the large-amplitude two-fold hop is in the fast limit of the  $^2\text{H}$  NMR timescale ( $\tau_c \leq 10^{-7}\text{ sec}$ ). At the highest temperature ( $77^\circ\text{C}$ ), the spectrum narrows significantly so that the breadth at half-height is  $\sim 110\text{ kHz}$ . The  $^2\text{H}$  NMR spectra of the fast  $T_1$  component in TDI-BDO and MDI-BDO are very similar. In fact at  $\sim 20^\circ$  and  $\sim 40^\circ\text{C}$ , the lineshapes from the two materials are virtually identical and fit reasonably well to the same calculated spectrum (Fig. 4 middle row and Fig. 2a,b). Thus, at least at these temperature, and for the fast component of the

We have obtained very precise  $T_1$  measurements of the fast component, at a variety of temperatures using the amorphous inversion-recovery quadrupole echo pulse sequence.<sup>14</sup> These experiments represent the rapidly decaying portion of the magnetization recovery curve; which data is reasonably linear out to 100 msec. The  $T_1$  values are summarized in an Arrhenius plot in Figure 3b. The plot shows a  $T_1$  minimum at  $\sim 45^\circ\text{C}$ . Since the  $T_1$  minimum occurs when  $\omega_0\tau_c \sim 1$ , this suggests that there are motions occurring with an average correlation time of  $\sim 2$  nsec at this temperature. A number of motional modes could contribute to the efficient spin lattice relaxation. The calculated spectra at this temperature (*vide supra*) require both the large scale conformational transition and a lower-amplitude libration for adequate simulation. The  $T_1$  data are summarized in Table 2.

**<sup>2</sup>H NMR Spectra of TDI-BDO:** The <sup>2</sup>H NMR spectra of the TDI-BDO polymer also reveals a broad distribution of correlation times at temperatures from  $-55^\circ\text{C}$  to  $40^\circ\text{C}$  (the glass transition temperature). This is demonstrated in Fig. 4 where we show spectra of TDI-BDO obtained using the amorphous quadrupole echo pulse sequence at several representative temperatures. The top row of lineshapes was obtained with an equilibrium delay time of 2 sec (4 sec for the  $-53^\circ\text{C}$  spectrum) between the saturating pulse train and the quadrupole echo pulse pair. Separate progressive saturation spin-lattice relaxation time ( $T_1$ ) experiments (*vide infra*), indicate that we are observing all the deuterons in TDI-BDO with this delay time at room temperature. In the second row, we show lineshapes obtained using the same pulse sequence except the delay time is shortened to 100 ms (160 ms for the  $-53^\circ\text{C}$  spectrum). These spectra are plotted on the same vertical scale as the top row lineshapes, and as we observed for MDI-BDO polymer, there is again a loss in intensity at the shorter delay time because of saturation of deuterons with long spin-lattice relaxation times. The relative intensity of the short  $T_1$  component is obtained by integration of the top and middle row spectra and the results are summarized in Table 1. The fraction of deuterons contributing to the

The respective calculated spectra were obtained by including a fast, small-amplitude diffusion of the butanediol chain in addition to the aforementioned gauche-trans conformational hops and small-angle librations of the methylene groups. The first and third motional modes cause a reduction in the breadth of the spectrum, while the second motional mode affects mainly the lineshape. We obtain reasonably good agreement between the observed and calculated spectra at 62° and 83°C if we assume that the butanediol moiety is diffusing within a cone whose semi-angle increases with increasing temperature, and that the C-D bond hops between two equally populated sites with a dihedral angle of 114°; via a gauche-trans conformational transition. We require cone angles of ~12° and ~16° to adequately fit the spectra at 62°C and 83°C, respectively (Figure 2c and 2d).<sup>21</sup>

We now consider the lineshapes of the fast component at reduced temperatures. These spectra have already been shown in the middle row of Figure 1a and b. The lineshape at -2°C is essentially identical to the room temperature spectrum, indicating that the deuterons contributing to this component are undergoing motion in the fast limit at -2°C. At -45°C, however, the pattern has a characteristic flat top; suggesting that the hopping motion has a correlation time in the intermediate exchange regime.

*Spin Lattice Relaxation Times of MDI-BDO:* Further evidence that there is a broad distribution of motional correlation times in the MDI-BDO material is provided by progressive saturation  $T_1$  results obtained at several temperatures, using a variable delay that spanned some 5 decades (10 sec to 100  $\mu$ sec). Representative data are shown in Figure 3a. In all cases, we were unable to adequately fit the entire magnetization recovery curves either to a single or a double exponential decay, even though the curves appear to be biphasic.

reorientation with a dihedral (jump) angle of  $\sim 109^\circ$ . Such a lineshape can arise from a gauche-trans conformational transition.<sup>18,19</sup>

Concentrating first on a simulation of the room temperature experimental spectrum, we varied the dihedral (jump) angle from  $102^\circ$  to  $118^\circ$ , and allowed the correlation time to go from the intermediate exchange regime to the rapid motion limit ( $\tau_c \leq 10^{-8}$  s). We assumed a quadrupole splitting of 120 kHz which we determined from the breadth at half height of the spectrum. This decrease from the rigid lattice value of 125 kHz is expected to arise from a fast libration of the methylene groups about their equilibrium positions. (We use *libration* to indicate a low-amplitude, high-frequency molecular motion.) These librational motions consist of a small torsional oscillation ( $\pm 10^\circ$ ) of the methylene group about a C-C bond. Using this single correlation time, single angle model, the best calculated lineshape is obtained with a jump angle of  $\sim 114^\circ$  with a correlation time in the rapid motion limit. Similar conditions obtain for the spectra at higher temperatures. The agreement between the calculated and experimental spectrum is good, given the simplicity of the model. However, note that the simulated spectrum has a small dip in the center and the shoulders are too narrow near the top. These imperfections are attributed to distributions in the frequencies of motion (*vide infra*).

We now address the lineshapes obtained at elevated temperatures. The lineshape obtained at  $42^\circ\text{C}$  (Figure 2b) is essentially identical to the room temperature spectrum except for a slight narrowing of  $\sim 2$  kHz. At  $62^\circ\text{C}$ , however, we observe further significant narrowing of the overall breadth of the pattern; which becomes even more pronounced at  $83^\circ\text{C}$  where the breadth (at half height) of the spectrum is only  $\sim 105$  kHz. This additional narrowing is attributed both to increasingly larger-amplitude librations of the methylene groups about their equilibrium positions, and to diffusion of the entire butanediol chain about its equilibrium position.<sup>20</sup>

*Figure 7.* Schematic representation of mechanisms for trans-gauche conformational transitions in the butanediol residues of MDI-BDO or TDI-BDO. (a) Newman projection showing a discrete isomerization about the central bond in the alkyl moiety. (b) Helfand-type models of motion about three bonds, involving gauche migration ( $tt_g^{\pm} \rightleftharpoons g^{\pm}tt$ ) and pair-gauche production ( $ttt \rightleftharpoons g^{\pm}t_g^{\mp}$ ).

TABLE 1

Percent of Polyurethane Samples Observed by  
Different NMR Pulse Delays

MDI-BDO			TDI-BDO		
Temperature (°C)	% in Rapid Motion <sup>a</sup>	% in Slow Motion <sup>b</sup>	Temperature (°C)	% in Rapid Motion <sup>a</sup>	% in Slow Motion <sup>b</sup>
-45	48 <sup>c,e</sup>	52 <sup>d,e</sup>	-53	48 <sup>c,e</sup>	52 <sup>d,e</sup>
-2	64 <sup>f</sup>	36 <sup>f</sup>	-6	69	31
22	69	31 <sup>d</sup>	22	79	21
55	70	30	40	84	16
73	71	29	78	95	5
123	67	33	93	100	0

- (a) Measured with the amorphous quadrupole echo pulse sequence,  $t_a = 100$  ms except as noted, estimated uncertainty  $\pm 2\%$ .
- (b) Obtained by difference methods. Quadrupole delay time  $t_a = 2$  s, unless noted otherwise.
- (c)  $t_a = 160$  ms
- (d)  $t_a = 4$  s
- (e) Estimated uncertainty  $\pm 8\%$ .
- (f) Estimated uncertainty  $\pm 4\%$ .

TABLE 2

Spin Lattice Relaxation Times<sup>a</sup> for Polyurethane Hard Segments

MDI-BDO			TDI-BDO		
Temperature (°C)	$T_1$ Fast Component (ms) <sup>b</sup>	$T_1$ Slow Component (ms) <sup>c</sup>	Temperature (°C)	$T_1$ Fast Component (ms) <sup>b</sup>	$T_1$ Slow Component (ms) <sup>c</sup>
-32	39	2000	-53	49	200
-3	23				
22			-7	28	
23	19.4		22		
42	18.3		23	21	
62	19.3	900	40		60
75					
83	20.7				

(a) Measured at 55.26 MHz for deuterium.

(b) Measured by inversion-recovery.

(c) Measured by progressive-saturation. Estimated uncertainty  $\pm 20\%$ .

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20. It is theoretically possible to account for the observed decrease in quadrupole splitting at high temperature by a model of only large amplitude ( $\sim \pm 30^\circ$ ) librations of the methylene groups about their equilibrium position. Such a model, however, introduces additional asymmetry into the electric field gradient tensor and results in a lineshape substantially different from that observed experimentally.
21. We assume that the rigid lattice quadrupole splitting (125 kHz) was reduced to  $\sim 120$  kHz by librations of the methylene group about their equilibrium positions. The quadrupole splittings were further narrowed by assuming a libration of the entire butanediol chain within a cone of semi-angle  $\theta_L$ . The reduction factor is given by  $(3 \cos^2 \theta_L - 1)/2$ .
22. We have calculated the spin-lattice relaxation time versus the correlation time for a two-fold jump motional model using the expression of Torchia and Szabo.<sup>25</sup> For a gauche-trans conformational transformation, we expect a  $T_1$  value of 5 msec at the minimum ( $\tau_c \sim 2$  nsec). For a low-amplitude ( $\pm 10^\circ$ ) libration, the predicted  $T_1$  at the minimum is 33 msec. Contributions to relaxation by other motions would decrease the observed  $T_1$  value. Since we observe a minimum  $T_1$  of  $\sim 20$  msec

(42°C), we conclude that fast librations are the dominant motional mode for relaxation at this temperature, with significant contributions from fast ( $\tau_c \sim 5 \times 10^{-8}$  sec) gauche-trans conformational hops.

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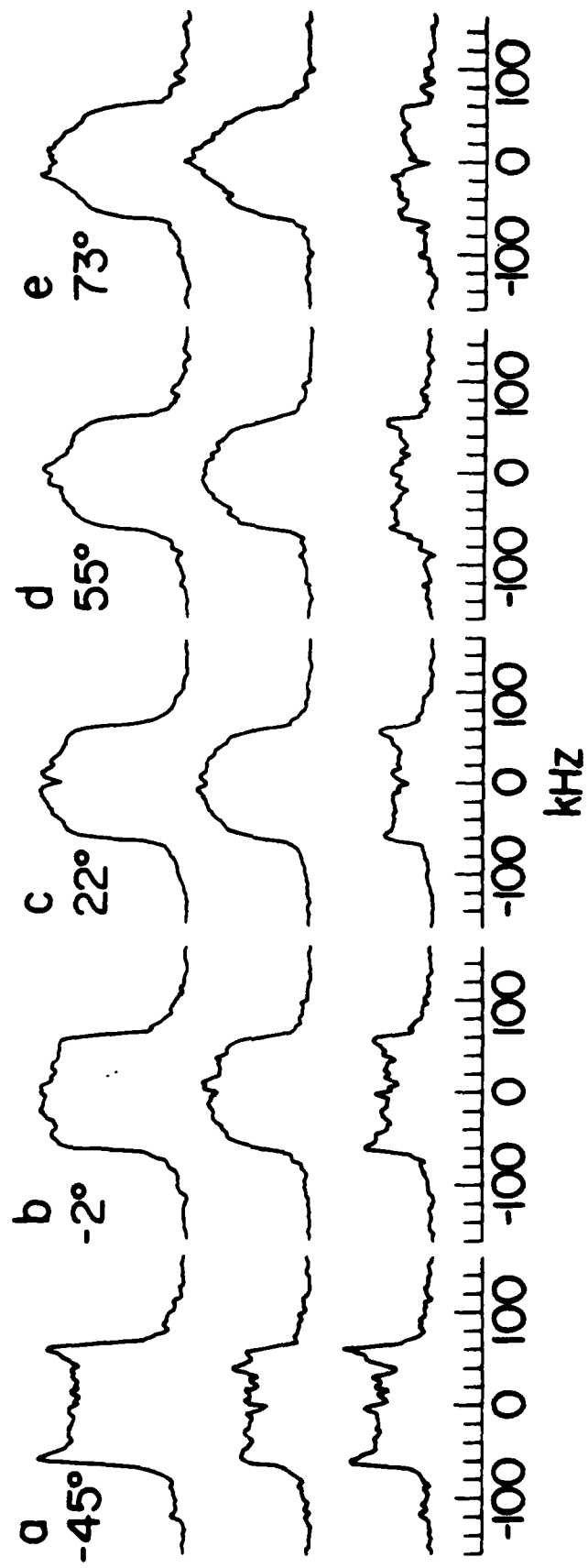


Figure 1

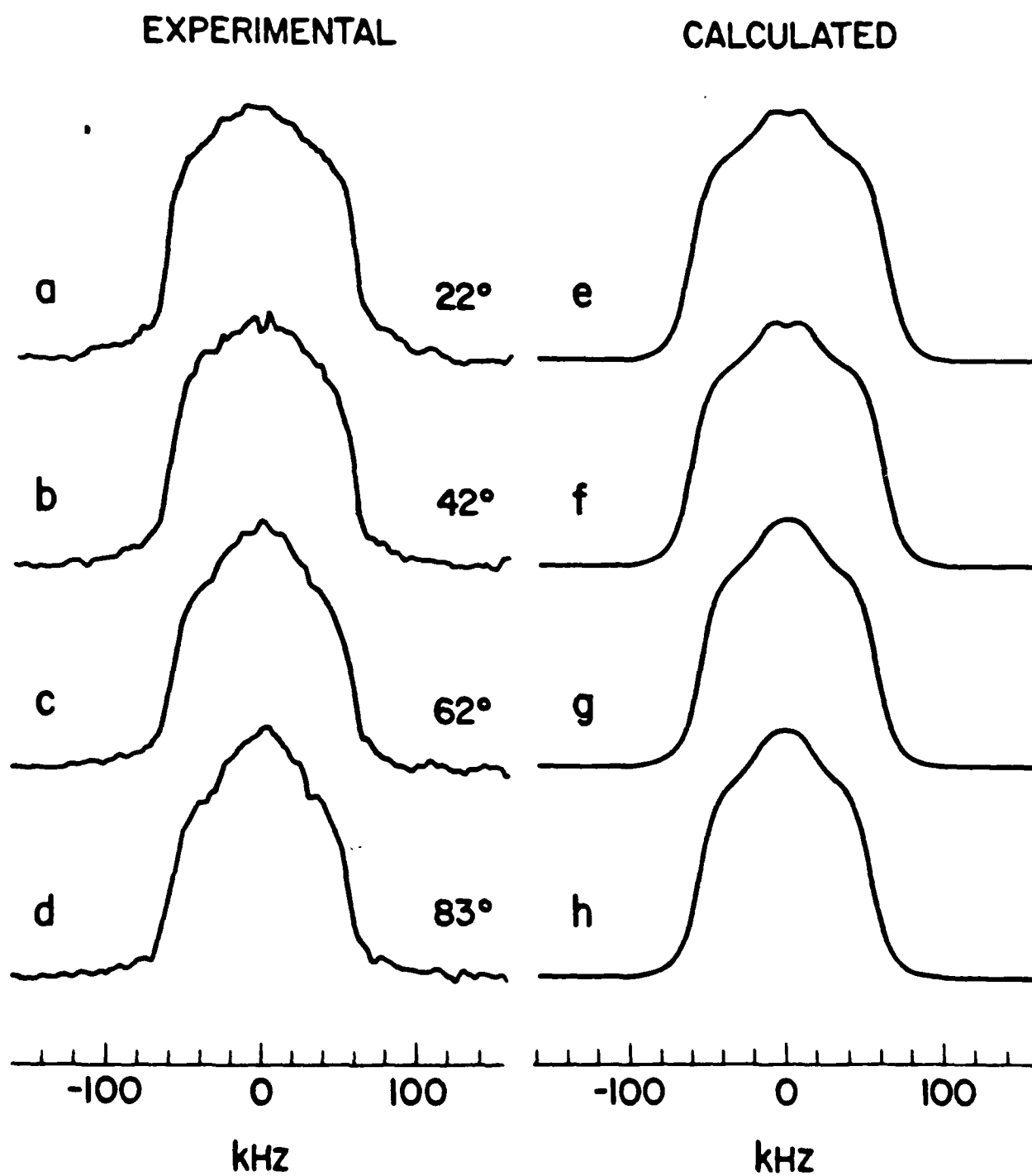


Figure 2

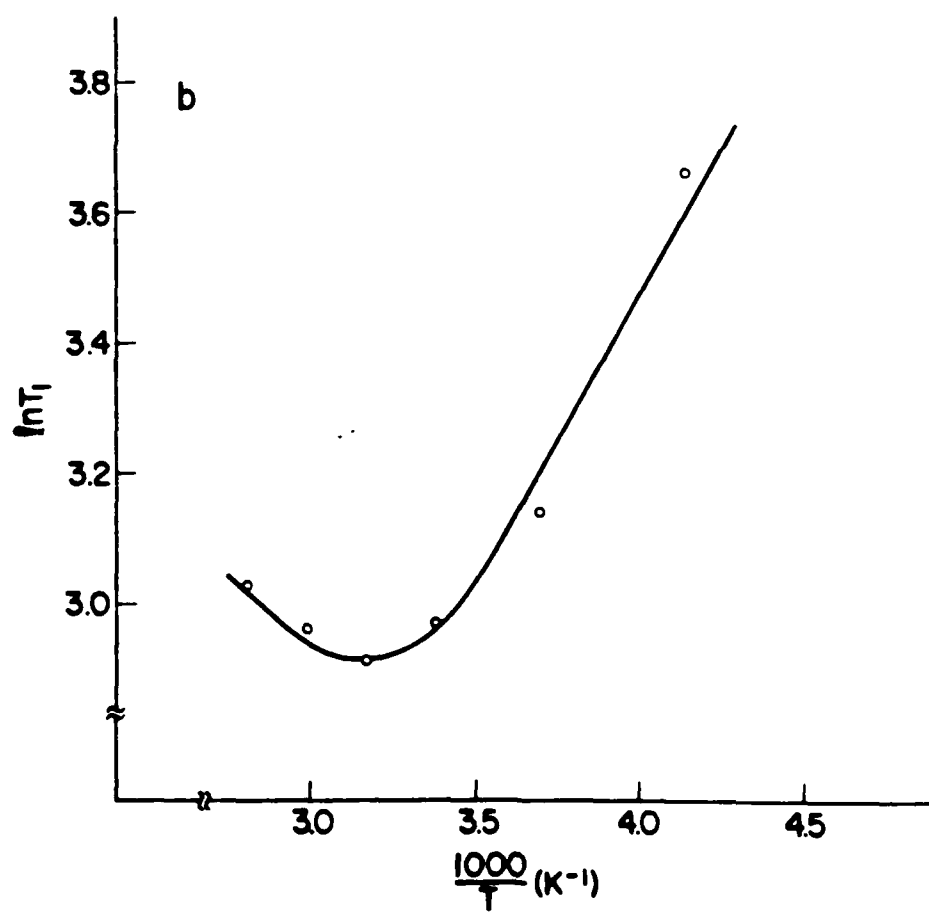
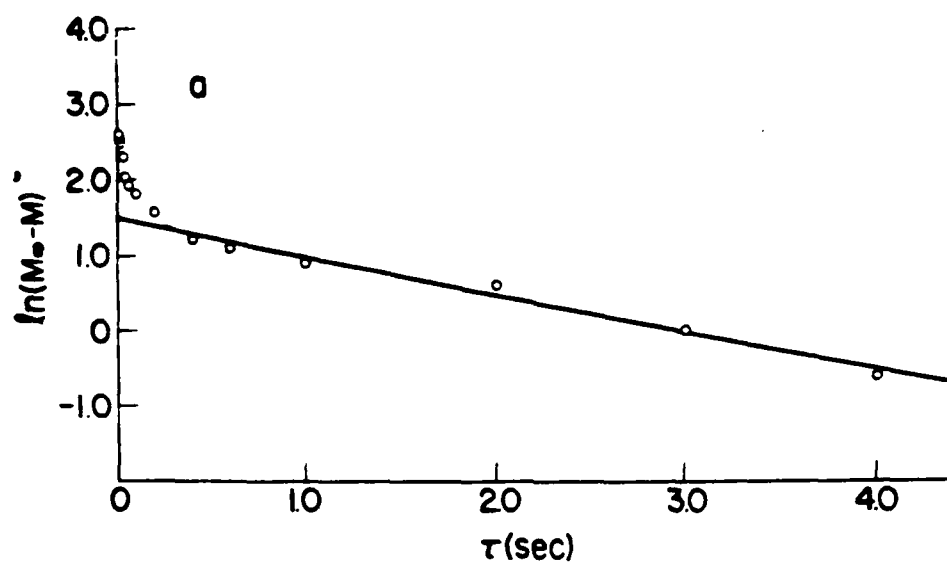


Figure 3

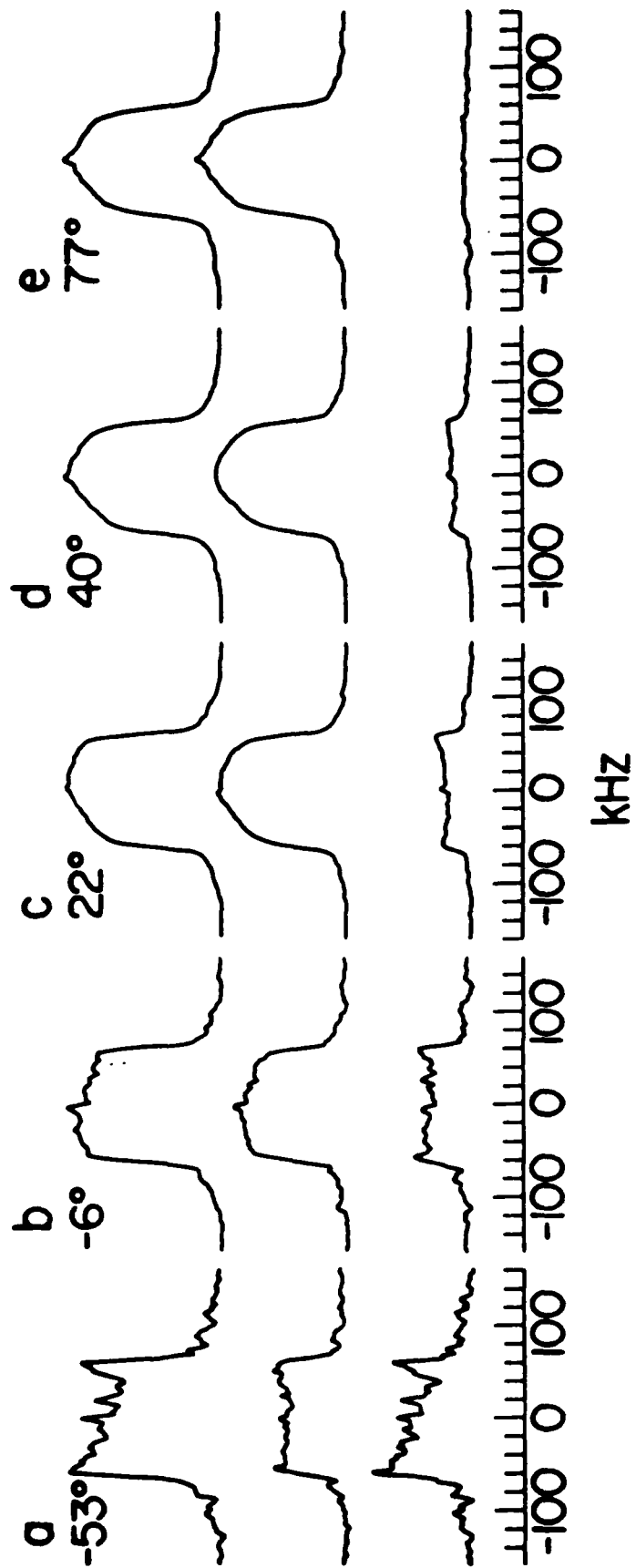


Figure 4

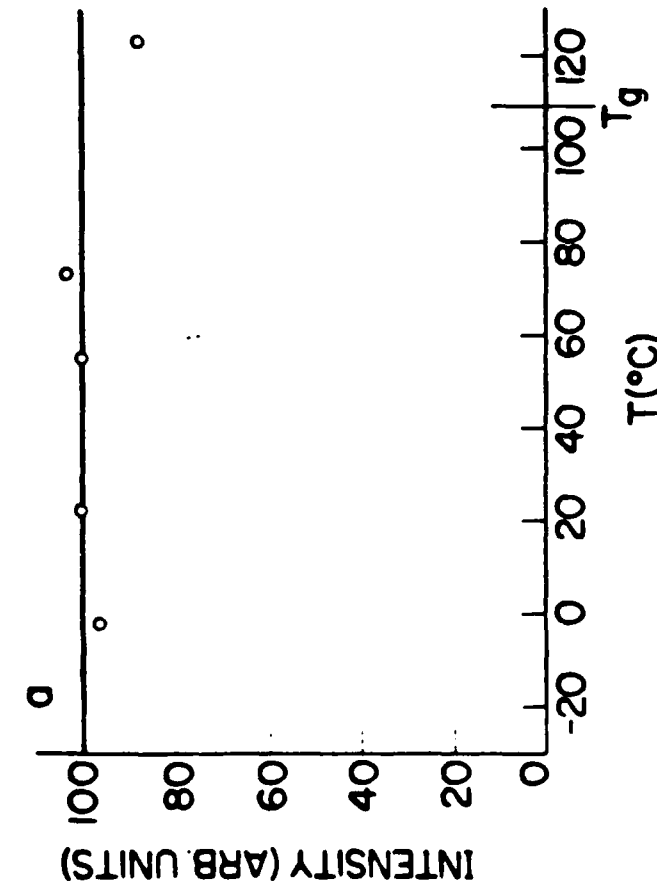
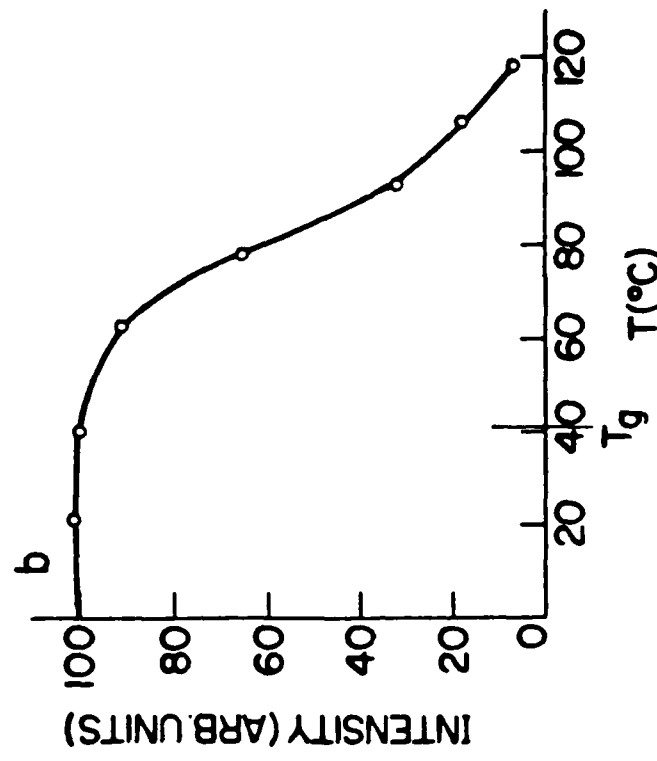


Figure 5

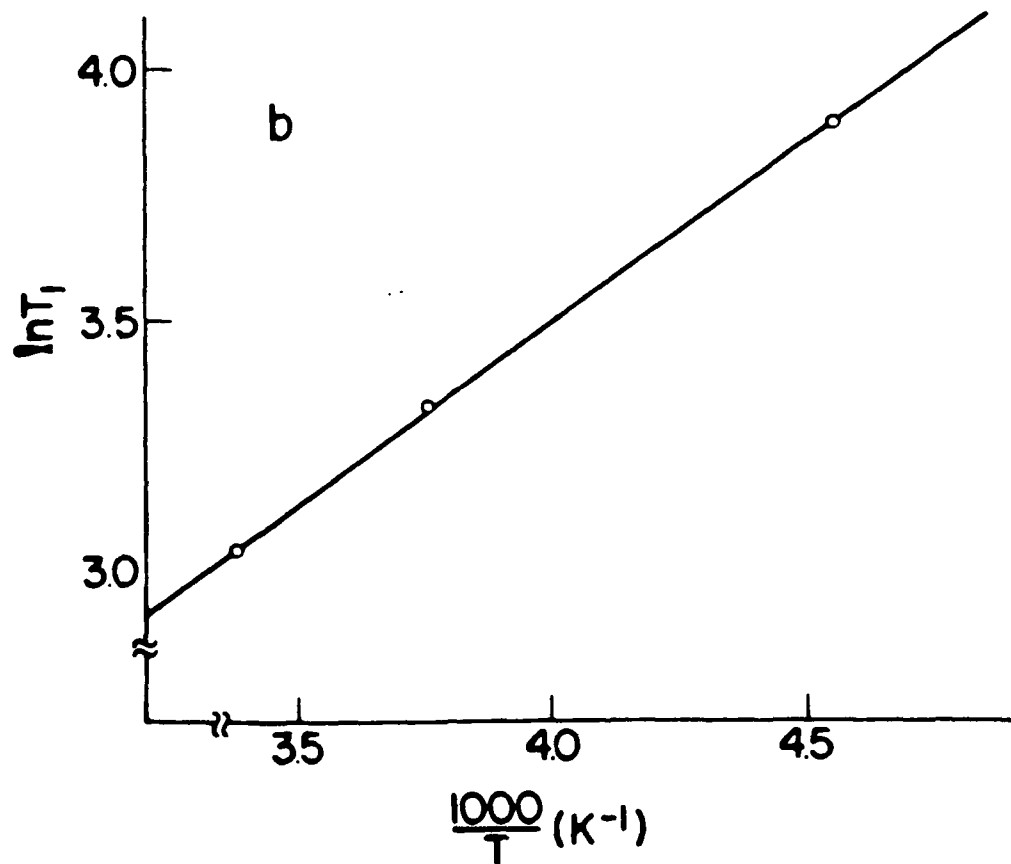
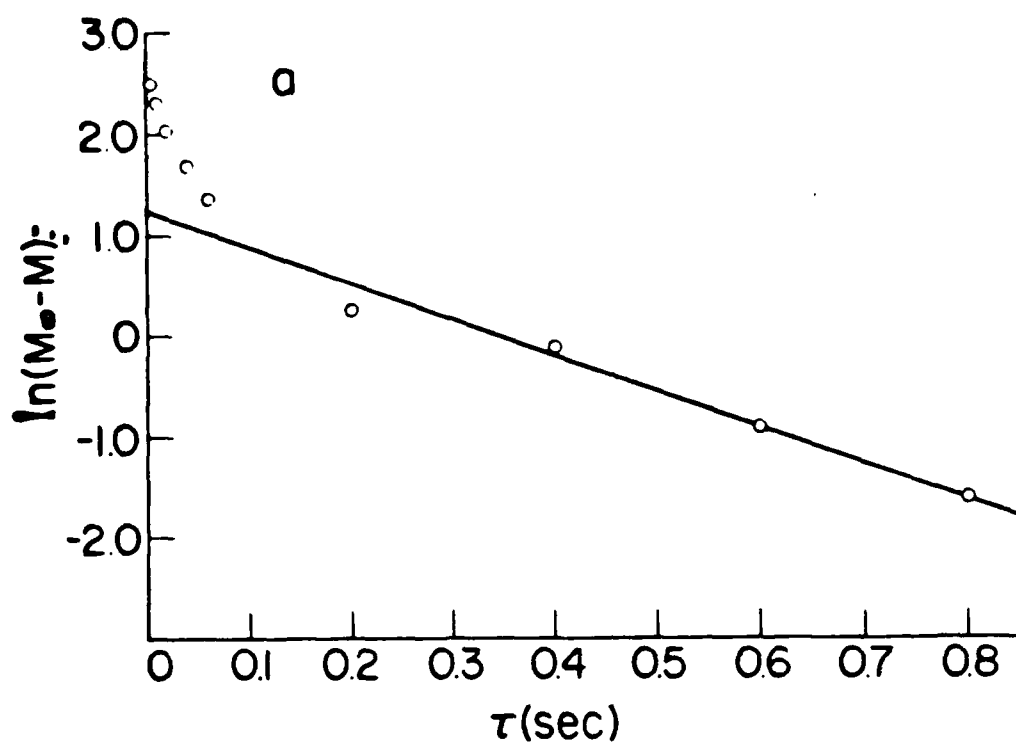
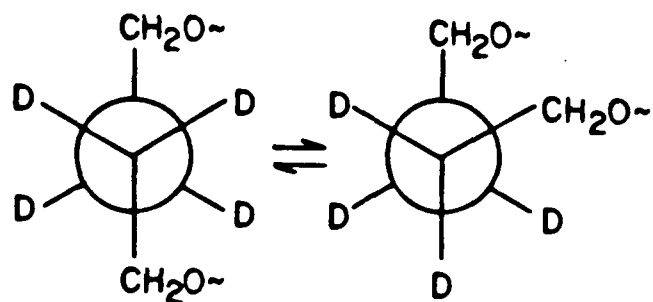


Figure 6



a



b

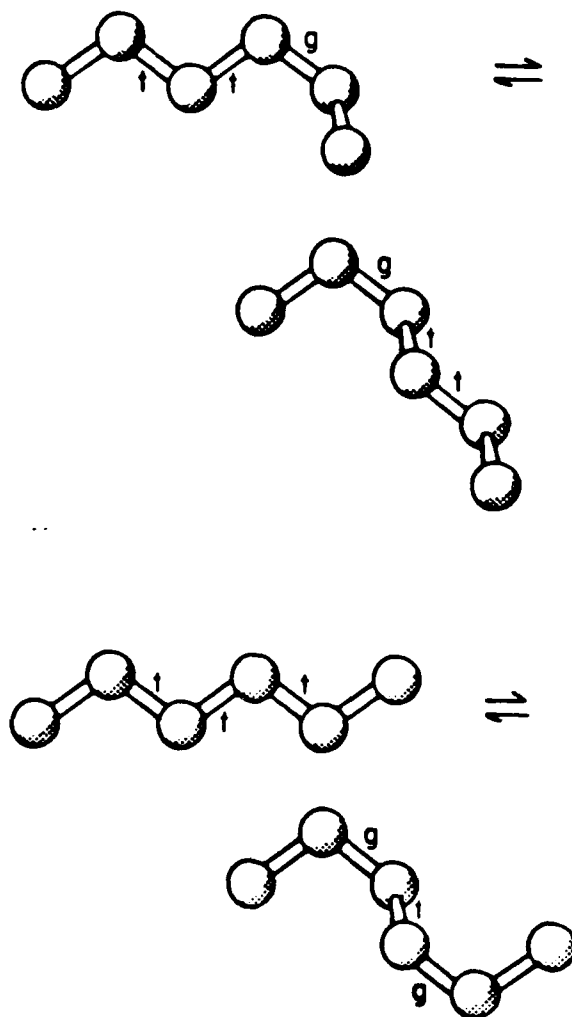


Figure 7

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